

THE CALCULATION OF PHASE DIAGRAMS IN THE LIQUID-GAS REGION¹

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ABSTRACT

The paper features the mathematical model of computing the thermophysical properties in the liquid, gas and two phase domain with the help of statistical thermodynamics. The paper features all important contributions (translation, rotation, internal rotation, vibration, intermolecular potential energy and influence of electron and nuclei excitation). To calculate the thermodynamic properties of real gases we developed the cluster theory which yields better results than the virial equation. For the realm of real liquids the Johnson-Zollweg-Gubbins model based on the modified BWR equation was applied. The Lennard – Jones inermolecular potential was used. The analytical results are compared with the experimental data and models obtained by classical thermodynamics and show relatively good agreement.

KEY WORDS: phase diagrams, liquid-gas equilibria, statistical thermodynamics, real gas, real liquid.

1. INTRODUCTION

This paper presents a mathematical model for computing the thermophysical properties using statistical thermodynamics. For real gases we developed a cluster theory, based on the principle of average clusters which yields better results than the virial equation. For real liquids the Johnson-Zollweg-Gubbins model based on the modified BWR and great number of Monte Carlo and molecular dynamics simulations was applied.

For the calculations in the two-phase region we applied the method of equilibrium conditions between two phases. The mathematical model enables the calculation in both sub- and supercritical region. Using the mathematical model described above we were able to compute thermophysical properties in the one and two-phase region and draw phase diagrams for some technically significant refrigerants.

2. COMPUTATION OF THERMODYNAMIC PROPERTIES OF THE STATE

Let us consider the system of N equal molecules of real gas or of real liquid. Molecules move either individually or in small instantaneous clusters [1]. The size and shape of the cluster changes due to the existence of intermolecular and intramolecular interactions between electrons and nuclei in the system.

The energy in such a molecules system consists of:

- kinetic energy of molecules and atoms
- intermolecular potential energy
- energy of electrons as to the energy level they belong to
- energy of nuclei as to the energy level they belong to.

To obtain an accurate calculation it would be necessary to solve the Schrödinger equation for several particles [2]:

$$\left(-\sum \frac{\hbar^2}{2m_i} \nabla_i^2 + \sum_{i < j} \frac{q_i q_j}{r_{ij}^2} \right) \psi = \frac{\hbar}{i} \frac{\partial \psi}{\partial t} \quad (1)$$

where the sums are taken over all nuclei and electrons with appropriate masses m_i and charges q_i .

Any solution of such a differential equation is a difficult task though reasonably accurate results can be obtained by means of some generalizations:

- intermolecular forces are much weaker than intramolecular forces, therefore both intramolecular forces and intermolecular forces can be treated quite independently;
- intermolecular potential energy depends only on the position of nuclei in space;
- the effect of the orientation of the molecule in space has been neglected;
- it is assumed that intermolecular potential is additive;
- each of the modes of motion is independent of the others.

In spite of the above mentioned simplifications the many-body Schrödinger equation (1) still constitutes a very hard task so we applied classical statistical thermodynamics to compute thermodynamic functions of the state. To calculate thermodynamic functions of state we applied the canonical partition [3]. Utilizing the semi-classical formulation for the purpose of the canonical ensemble for the N indistinguishable molecules can be expressed as follows [3]:

$$Z = \frac{1}{N! h^{Nf}} \int \dots \int \exp\left(-\frac{H}{kT}\right) \cdot d\vec{r}_1 d\vec{r}_2 \dots d\vec{r}_N d\vec{p}_1 d\vec{p}_2 \dots d\vec{p}_N \quad (2)$$

where f stands for the number of degrees of freedom of individual molecule, H designates the Hamiltonian molecule system. The canonical ensemble for the system of N molecules can be like this:

$$Z = Z_0 Z_{\text{trans}} Z_{\text{vib}} Z_{\text{rot}} Z_{\text{ir}} Z_{\text{el}} Z_{\text{nuc}} Z_{\text{conf}} . \quad (3)$$

Thus the partition function Z is a product of terms of the ground state (0), the translation (trans), the vibration (vib), the rotation (rot), the internal rotation (ir), the influence of electrons excitation (el), the influence of nuclei excitation (nuc) and the influence of the intermolecular potential energy (conf).

Utilizing the canonical theory for computing the thermodynamic functions of the state can be put as follows [4]:

$$\text{Pressure: } p = kT \left(\frac{\partial \ln Z}{\partial V} \right)_T, \quad \text{internal energy: } U = kT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_V,$$

$$\text{free energy: } A = -kT \cdot \ln Z, \quad \text{Entropy: } S = k \left[\ln Z + T \left(\frac{\partial \ln Z}{\partial T} \right)_V \right].$$

The computation of the individual terms with the exception of the configurational integral of the partition function and their derivatives is dealt with in the works of Lucas [3,4].

3. CONFIGURATIONAL INTEGRAL

For reasons of its characteristics of the problem the methods for solving the configurational integral in the liquid - gas region are generally divided most crudely, into solving the configurational integral for real gases and for real liquids.

In real gas there are relatively weak intermolecular forces. The real gas molecules move either individually or in small instantaneous and random clusters. To solve the configurational integral we devised a method of clusters [1]. The method is based on the principle of average clusters.

By dealing with a sufficiently large number N of molecules in the system an average cluster of N_1 molecules can be determined. Figure 1 features the outline of the idea of the method of clusters illustrating the activity of intermolecular forces in clusters as well as the activity of intermolecular forces between clusters.

The analyze of the motion of molecules by means of the Monte Carlo method [5] indicate the fact that the number of molecules in the average cluster is relatively low. The number of molecules in the average cluster depends on the average intermolecular distance.

Thus the ideal gas can for instance have one molecule in any of the clusters that are, dispersed at such distances that the intermolecular forces are negligible.

The principal idea of the method of clusters stipulates that the intermolecular potential energy of the system can be split up to intermolecular potential energy in clusters (E_{pot1}) and intercluster potential energy due to interactions between clusters (E_{pot2}). Therefore the potential intermolecular energy can be written as the sum of both parts:

$$E_{\text{pot}} = E_{\text{pot1}} + E_{\text{pot2}} . \quad (7)$$

On hand of the suppositions from the previous chapter the configurational integral can then be put as follows:

$$Z_{\text{conf}} = Z_{\text{conf1}} Z_{\text{conf2}} . \quad (8)$$

When computing the configurational integral Z_{conf1} the effects of mutual interactions of up to three molecules in the cluster were taken into account. For the intermolecular potential the Lennard-Jones potential was applied. The configurational integral Z_{conf1} that takes interactions in clusters into account can be written [6,7,8]:

$$Z_{\text{conf1}} = \left(\frac{1}{V_1} \right)^N \left[\iiint_{V_1} 1 + \sum f_{ij} + \sum (f_{ij}f_{kl}) + \dots \right]^{\frac{N}{N_1}}, \quad (9)$$

$$V_1 = \frac{N_1}{N} V. \quad (10)$$

Equation (9) can also be put like this [7]:

$$\ln Z_{\text{conf1}} = \frac{N}{N_1} \cdot \ln \left(1 + \frac{(N_1 - 1)NI_1}{2V} + \frac{N^2 \left(1 - \frac{1}{N_1} \right) (N_1 - 2)I_2}{6V^2} \right) \quad (11)$$

$$I_1 = \frac{N_1}{V} \cdot \iint f_{ij} \cdot d\vec{r}_1 \cdot d\vec{r}_2, \quad I_2 = \frac{N_1}{V} \iiint [3f_{ij} \cdot f_{kl} + f_{ij} \cdot f_{kl} \cdot f_{mn}] \cdot d\vec{r}_1 \cdot d\vec{r}_2 \cdot d\vec{r}_3, \quad (12)$$

where f is the Mayer function [2].

Integral I_1 for the case of the Lennard-Jones potential is solved by literature [7,8,9].

Integral I_2 was transformed by A.Münster [7] as follows:

$$I_2 = 3I_1^2 + I_{21}, \quad I_{21} = \frac{N_1}{V} \iiint f_{ij} \cdot f_{kl} \cdot f_{mn} \cdot d\vec{r}_1 \cdot d\vec{r}_2 \cdot d\vec{r}_3. \quad (13)$$

Integral I_{21} is resolved in the works L.E. Reichl [9] and Hirschfelder, Curtiss and Bird [8] for the case of the Lennard-Jones potential. The effect of the intercluster interaction can be presented by the configurational integral Z_{conf2} which takes the mutual interactions of two clusters in the system.

$$Z_{\text{conf}2} = \frac{1}{V^{\frac{N}{N_1}}} \iint \dots \int \exp\left[-\frac{U_{ij}}{kT}\right] d\vec{r}_1 d\vec{r}_2 \dots d\vec{r}_{N/N_1} \quad (14)$$

where U_{ij} stands for the potential energy between i - and j - clusters. Applying Bird's method, [8] in the case of diluted systems can be put like this:

$$U_{ij} = N_1^2 u_{ij}, \quad (15)$$

where u_{ij} stands for the potential energy between molecule in the cluster i and molecule in the cluster j . Utilizing the above and taking only the mutual interaction of two clusters in the system we can write:

$$F_{ij} = \exp\left(-\frac{U_{ij}}{kT}\right) - 1, \quad I_1^* = \frac{1}{V} \iint F_{ij} \cdot d\vec{r}_1 \cdot d\vec{r}_2, \quad N_2 = \frac{N}{N_1}, \quad (16)$$

where N_2 and F_{ij} are the number of clusters in the system, and the Mayer's function. Integral I_1^* can be solved in the same way as I_1 .

$$\ln Z_{\text{conf}2} = + \frac{N_2^2}{2V} I_1^*, \quad (17)$$

To determine the number of molecules in an average cluster of real gas we took advantage of the experimental results of thermodynamic functions of the state obtained by J.B. Maxwell [10], W.C. Edmister [11], as well as J.A. Barker [5] results of simulation by means of the Monte Carlo method. After a thorough analysis the number of molecules in individual average cluster was established: $1 < N_1 < 6$.

For a real liquid Johnson-Zollweg-Gubbins (JZG) [12] model based on molecular dynamic and Monte Carlo simulations with the Lennard-Jones intermolecular potential and

modified Benedict-Webb-Rubin equation of state (MBWR) was used. On this basis we can express configurational free energy A_{conf} :

$$A_{\text{conf}}^* = \sum_{i=1}^8 \frac{a_i \rho_i^*}{i} + \sum_{i=1}^6 b_i G_i, \quad (18)$$

$$\rho^* = \frac{N\sigma^3}{V}, \quad T^* = \frac{kT}{\epsilon}, \quad A_{\text{conf}}^* = \frac{A_{\text{conf}}}{N\epsilon}, \quad F = \exp(-\gamma \rho^{*2}), \quad \gamma=3. \quad (19)$$

Equation (18) accurately correlates thermophysical properties from the triple point to about 4 to 5 times the critical temperature. In equation (18) are x_j 's the adjustable parameters in the equation of state.

4. DETERMINING THE EQUILIBRIUM STATES BETWEEN LIQUID AND VAPOUR

Determining the equilibrium states between the liquid and the gaseous phases conditions for equilibrium are applied:

$$T' = T'', \quad p' = p'', \quad \mu' = \mu'', \quad (20)$$

where ' in equation (20) means the liquid phase, '' means the gaseous phase and μ constitutes the chemical potential.

Due to the mathematical complexity of the equations in the model, the states on the coexistence curve are obtained numerically. By applying these states, thermodynamic properties in the two phase environment can be calculated.

5. RESULTS AND COMPARISON WITH EXPERIMENTAL DATA

In the two-phase region the computation of thermodynamic functions of state are based on the mixing. Figures 2, 3 and 4 illustrate the phase diagrams of the state computed by means of the mathematical model. The figures 2 shows the creation of phase diagrams in the liquid, gas and two-phase regions for benzene (C_6H_6). Figure 3 shows the creation of phase diagrams (enthalpy, entropy, free enthalpy) depending on volume by means of numerical simulations for acetylene (R 1150). Figure 4 shows the creation of phase diagrams (enthalpy) depending on volume by means of numerical simulations for methane (R 50).

The constants necessary for the computation such as the characteristic rotation-, vibration-, electronic- etc. temperatures are obtained from experimental data [13,14,15]. The inertia moments are obtained analytically by applying the knowledge of the atomic structure of the molecule. Constants for Lennard-Jones potential are obtained from the literature [2,8].

6. CONCLUSION AND SUMMARY

The paper presents the mathematical model for computation of thermodynamical functions of the state in the liquid, gaseous and two-phase region.

For the region of real gases we developed the method of clusters based on the average cluster with N_1 molecules in the system with N molecules. For the real liquid the Johnson-Zollweg-Gubbins model based on molecular dynamic and Monte Carlo simulations and modified Benedict-Webb-Rubin equation of state (MBWR) was applied. The boiling curve and the saturation curve was determined by means of equilibrium conditions.

NOMENCLATURE

A	free energy
CT	cluster theory
E	potential energy
f	Mayer function
g	radial distribution function
G	free enthalpy
H	enthalpy, hamiltonian
h, \hbar	Planck constant
I_1, I_2, I_1^*	integrals
JZG	Johnson, Zollweg, Gubbins
k	Boltzmann constant
N	number of molecules in system
N_1	number of molecules in cluster
p	pressure, momentum
S	entropy
t	time
T	temperature
U	internal energy
V	volume
Z	partition function
μ	chemical potential

ψ wave function

ρ density

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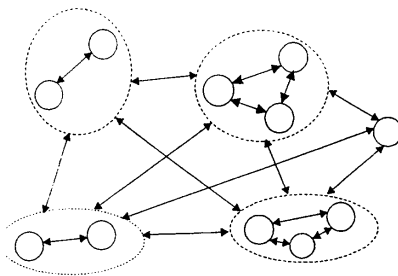
FIGURES

Fig. 1: Schematic outline of clusters.

1-T=290 K	2-T=333 K	3-T=373 K
4-T=413 K	5-T=453 K	6-T=503 K

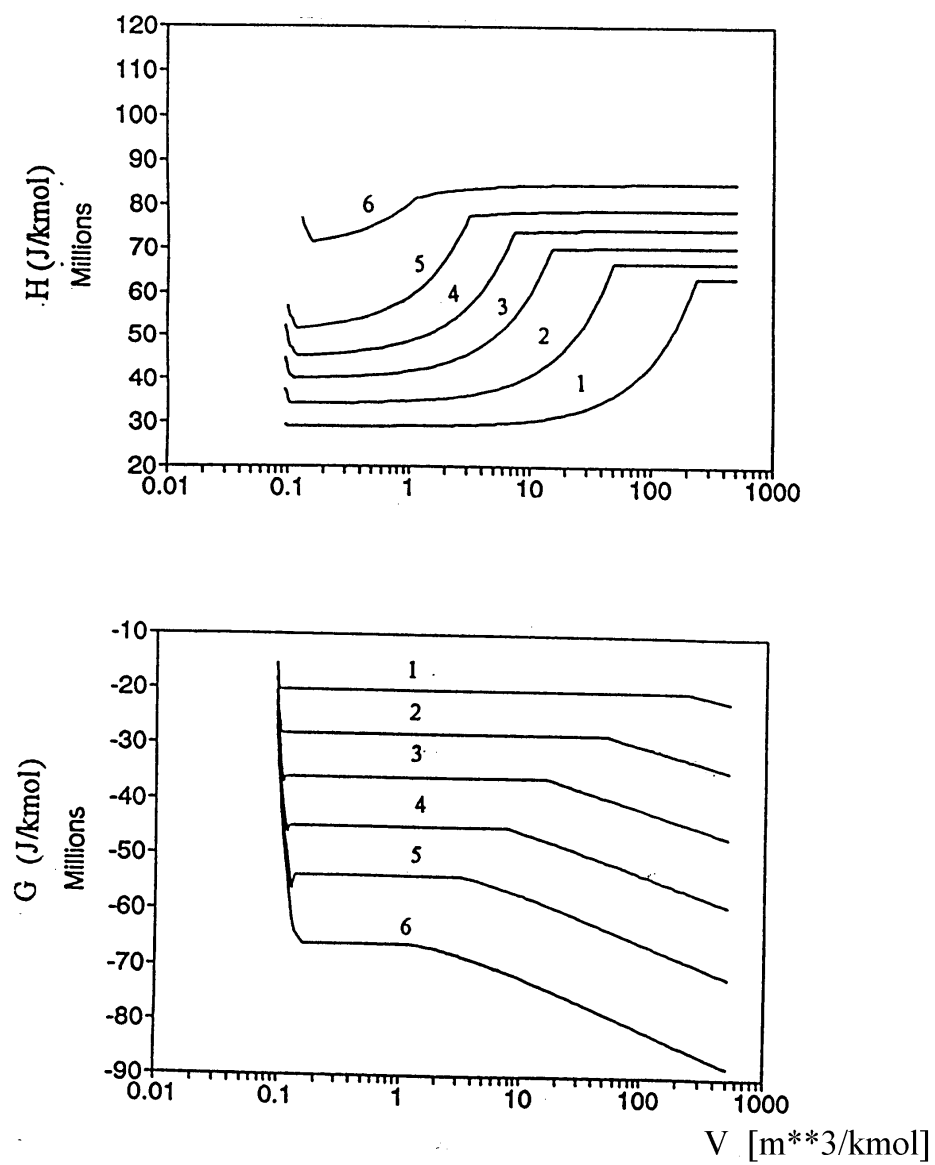


Fig. 2. Enthalpy and free enthalpy in one- and two- phase region for C_6H_6

1-T=166 K	2-T=188 K	3-T=210 K
4-T=222 K	5-T=255 K	6-T=282 K

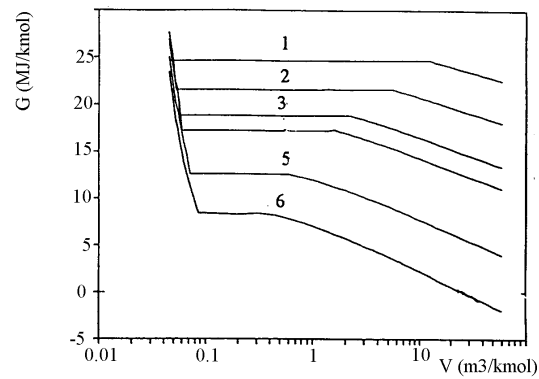
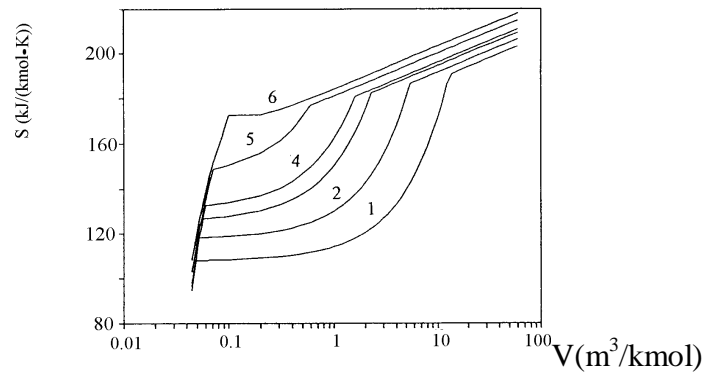


Fig. 3: Entropy, and free enthalpy in one- and two-phase region for acetylene (R 1150)

1-T=122 K	2-T=133 K	3-T=144 K
4-T=190 K	5-T=250 K	

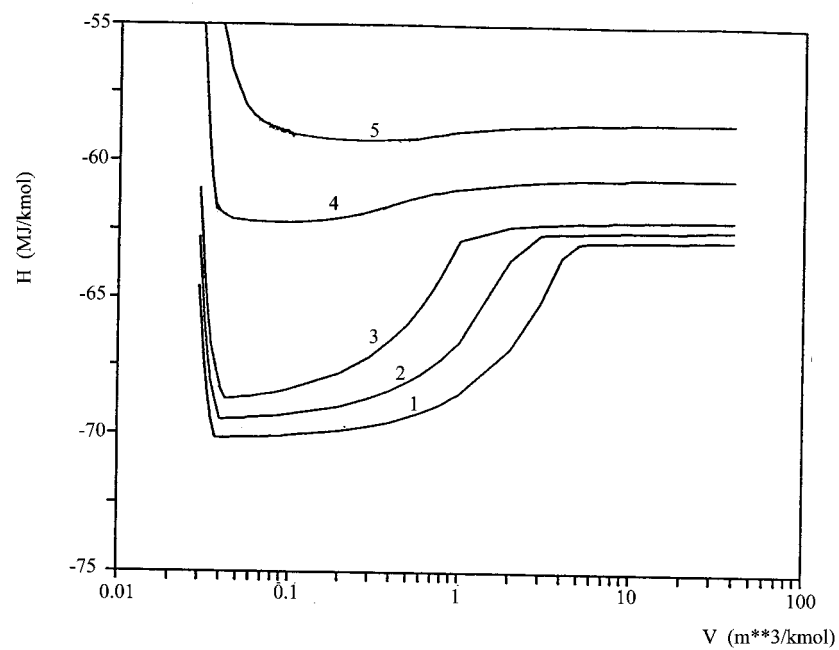


Fig 4: Enthalpy in one- and two-phase region for methane (R 50)